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(54) HONEYCOMB STRUCTURE AND METHOD FOR PRODUCING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a honeycomb structure which can be inexpensively produced at a relatively low firing temperature although it contains fire resistant particles such as silicon carbide particles, has high strength and high resistance to thermal impact and can be suitably used as a filter for cleaning an exhaust gas from an automobile or a catalyst carrier, or the like, even under a high SV condition after being subjected to seal treatment or the like.
SOLUTION: The honeycomb structure has a plurality of passage holes, each being partitioned by a partition wall formed from a silicon carbide porous body and perforating in the axis direction. The strength and Young's modulus of the silicon carbide porous body satisfy following relation: strength (MPa)/ Young's modulus (GPa) $\geq$1.1.

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CLAIMS

[Claim(s)]
[Claim 1] The honeycomb structure object which is a honeycomb structure object which has the circulation hole of a large number penetrated to the shaft orientations divided by the septum which consists of a nature porous body of silicon carbide, and is characterized by the reinforcement and Young's modulus of said nature porous body of silicon carbide filling the following relation.
[Equation 1] reinforcement (MPa) / Young's modulus (GPa) >=1.1 -- [Claim 2] The honeycomb structure object according to claim 1 with which the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation.
[Equation 2]
reinforcement (MPa) / Young's modulus (GPa) >=1.25 -- [Claim 3] The honeycomb structure object according to claim 1 with which the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation.
[Equation 3]
reinforcement (MPa) / Young's modulus (GPa) >=1.3 -- [Claim 4] A honeycomb structure object given in any 1 term of claims 1-3 containing the silicon carbide particle from which the nature porous body of silicon carbide serves as the aggregate, and the metal silicon with which it becomes binding material.
[Claim 5] In a silicon carbide particle raw material, add metal silicon and an organic binder, and the plastic matter mixed, and kneaded and obtained is fabricated in a honeycomb configuration. In the manufacture approach of the honeycomb structure object which carries out actual baking after carrying out temporary quenching of the acquired Plastic solid and removing the organic binder in this Plastic solid The manufacture approach of a honeycomb structure object that the addition of said metal silicon is characterized by being 15 - 40% of the weight of the range to the total quantity of said silicon carbide particle raw material and metal silicon.
[Claim 6] The manufacture approach of a honeycomb structure object according to claim 5 of carrying out said this baking in a 1400-1600-degree C temperature requirement.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the honeycomb structure object used for a filter, catalyst support, etc. for automobile exhaust purification, and its manufacture approach.
[0002]
[Description of the Prior Art] The porous honeycomb structure object is widely used as catalyst support for supporting the catalyst component which purifies the filter for carrying out uptake removal of the particulate matter contained in dust-containing fluid like diesel-power-plant exhaust gas, or the harmful matter in exhaust gas. Moreover, using a fireproof particle like a silicon carbide (SiC) particle as a component of such a honeycomb structure object is known.
[0003] As a concrete related technique, the silicon carbide powder which has a predetermined specific surface area and a predetermined impurity content is used as a start raw material, and the nature catalyst support of porosity silicon carbide of the honeycomb structure calcinated and acquired by the configuration of a request of this after shaping and desiccation in a 1600-2200-degree C temperature requirement is indicated by JP,6-182228,A.
[0004] A vitrification material adds to the fireproof constituent which, on the other hand, contains an easy-oxidizable material or an easy-oxidizable material in JP,61-26550,A, and the silicon-carbide

Plastic solid with which the manufacture approach of the vitrification material content refractories characterized by to carry out nakedness baking of the Plastic solid mixed, kneaded, and fabricated and fabricated in the furnace of a non-oxidizing atmosphere adds and fabricates an organic binder and the inorganic binder of a clay mineral system, textile glass yarn, and a silicic-acid lithium system to silicon-carbide powder at JP,8-165171,A is indicated with binding material, respectively.
[0005] Moreover, after adding and fabricating binding material, such as glassiness flux or argillaceous, to the silicon carbide particle used as the aggregate as the manufacture approach of the conventional nature sintered compact of porosity silicon carbide, the method of burning, hardening and manufacturing the Plastic solid at the temperature which said binding material fuses is also introduced to said JP,6-182228,A.
[0006] furthermore, to JP,61-13845,B and JP,61-13846,B Silica sand, a pottery grinding object, aluminum2O3, TiO2, the metallic oxide of ZrO2 grade, The fireproof particle by which the particle size regulation was carried out to the predetermined grain size which consists of silicon carbide, a nitride, boride, or other fireproof ingredients The suitable fireproof particle pitch diameter, fireproof particle particle size distribution, tube-like object porosity, a tube-like object average pole diameter, tube-like object pore volume, tube-like object septum thickness, etc. are indicated about the high-temperature-service ceramic filter formed in the porous cylinder-like-object-with-base-like object with fireproof binding material, such as water glass, a frit, and a cover coat.
[0007]
[Problem(s) to be Solved by the Invention] Although a silicon carbide component evaporates from a silicon carbide particle front face, the neck section grows because this condenses in the contact section between particles (neck section), and an integrated state is obtained with the sintering gestalt (necking) by the recrystallization reaction of the silicon carbide powder itself shown in said JP,6-182228,A In order for this to have to cause cost quantity since a very high burning temperature is required, and to evaporate silicon carbide and to have to carry out elevated-temperature baking of the ingredient with a high coefficient of thermal expansion, there was a problem that a baking yield fell.
[0008] Furthermore, while it is possible to obtain the porous body of high intensity according to the aforementioned approach, it will originate in the physical property of the silicon carbide which is an ingredient, and the porous body which shows a numeric value with high Young's modulus will be obtained.
[0009] Generally, a heat-resistant impact destructive drag coefficient (R) is shown by the following formula (1). Here, for S, disruptive strength and nu are [Young's modulus and alpha of a Poisson's ratio and E] coefficients of thermal expansion. nu and alpha are the numeric values of an ingredient proper, and if it is the same ingredient, while most change is values which are not accepted, they is numeric values sharply changed by the porosity of the ingredient, a microstructure organization, etc. about S and E.
R=S(1-nu)/Ealpha -- (1)
[0010] Although thermal shock resistance was proportional to reinforcement as the above-mentioned formula (1) was shown, by the manufacture approach of the sintered compact shown in JP,6-182228,A since it is in inverse proportion to Young's modulus, there was a problem that the sintered compact which has sufficient thermal shock resistance could not be manufactured even if it is high intensity, since the value of Young's modulus becomes high.
[0011] The technique of on the other hand combining the coal-for-coke-making-ized silicon powder shown in JP,61-26550,A or JP,6-182228,A by glassiness Although it is low and ends with 1000-1400 degrees C as a burning temperature for example, in using as an ingredient of the diesel particulate filter (DPF) for removing the particulate contained in the exhaust gas discharged from a diesel power plant in the sintered compact produced by this technique When it was going to burn the particulate which the collection was carried out to the filter and deposited for filter playback, since thermal conductivity was small, there was a trouble that local generation of heat arose.
[0012] Furthermore, although the filter shown in JP,61-13845,B and JP,61-13846,B was porosity, septa are 5-20mm and a thick cylinder-like-object-with-base-like object, and were not able to apply it to the bottom of a high SV (space velocity) condition like the filter for automobile exhaust purification.
[0013] This invention has high reinforcement and thermal shock resistance, and aims at offering the

honeycomb structure object which can be suitably used also under high SV conditions as the filter for automobile exhaust purification, or catalyst support by processing of ****** etc., and its manufacture approach while being able to manufacture it cheaply with a comparatively low burning temperature, though it is made in view of such a conventional situation and a fireproof particle like a silicon carbide particle is included.

[0014]

[Means for Solving the Problem] That is, according to this invention, it is the honeycomb structure object which has the circulation hole of a large number penetrated to the shaft orientations divided by the septum which consists of a nature porous body of silicon carbide, and the honeycomb structure object characterized by the reinforcement and Young's modulus of said nature porous body of silicon carbide filling the following relation is offered.

[Equation 4] Reinforcement (MPa) / Young's modulus (GPa) >=1.1[0015] In this invention, it is desirable that the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation.

[Equation 5]

Reinforcement (MPa) / Young's modulus (GPa) >=1.25[0016] Furthermore, in this invention, it is desirable that the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation. In addition, in this invention, it is desirable that the silicon carbide particle from which the nature porous body of silicon carbide serves as the aggregate, and the metal silicon with which it becomes binding material are included.

[Equation 6] Reinforcement (MPa) / Young's modulus (GPa) >=1.3[0017] On the other hand, according to this invention, add metal silicon and an organic binder in a silicon carbide particle raw material, and the plastic matter mixed, and kneaded and obtained is fabricated in a honeycomb configuration. In the manufacture approach of the honeycomb structure object which carries out actual baking after carrying out temporary quenching of the acquired Plastic solid and removing the organic binder in this Plastic solid The manufacture approach of the honeycomb structure object characterized by the addition of said metal silicon being 15 - 40% of the weight of the range to the total quantity of said silicon carbide particle raw material and metal silicon is offered.

[0018] In addition, in this invention, it is desirable to carry out this baking in a 1400-1600-degree C temperature requirement.

[0019]

[Embodiment of the Invention] The honeycomb structure object of this invention is constituted by the nature porous body of silicon carbide, and it is set up and produced so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the following relation.

[Equation 7] Reinforcement (MPa) / Young's modulus (GPa) >=1.1[0020] As mentioned above, thermal shock resistance is important in order that holding down the value of Young's modulus as compared with a strong value since it is in inverse proportion to the value of Young's modulus may improve the thermal shock resistance of a honeycomb structure object. If it is going to burn the particulate which thermal shock resistance was [the particulate] low when the above-mentioned numeric value was less than 1.1, for example, the collection was carried out to the filter for filter playback when it used as a diesel particulate filter (DPF) for removing the particulate contained in the exhaust gas discharged from a diesel power plant in this ingredient, and was deposited, since there is a possibility of damaging depending on the case, according to the rapid temperature gradient produced in a filter, it is not desirable. In the honeycomb structure object concerning this invention, since the ratio of the reinforcement which is the physical-properties value of the nature porous body of silicon carbide which constitutes it, and Young's modulus is set as the relation of the above-mentioned formula, the outstanding thermal shock resistance is shown.

[0021] Moreover, if it sets up so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the following relation, since still better thermal shock resistance is obtained, it is desirable.

[Equation 8]

Reinforcement (MPa) / Young's modulus (GPa) >=1.25[0022] Furthermore, if it sets up so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the

following relation, especially since sufficient thermal shock resistance is obtained, it is desirable.
[Equation 9] Reinforcement (MPa) / Young's modulus (GPa) >=1.3[0023] In addition, when using the honeycomb structure object concerned as DPF etc. is assumed, the reinforcement of the nature porous body of silicon carbide and the relation of Young's modulus can be used satisfactory, if it sets up so that the following type may be filled in general.
[Equation 10]
Reinforcement (MPa) / Young's modulus (GPa) <=4.0[0024] Since distortion becomes gradually large in the process which distortion may produce in the honeycomb structure constituted by that Young's modulus is low although it is desirable from a viewpoint of thermal shock resistance when the numeric value in the above-mentioned formula exceeds 4.0 by the nature porous body of the silicon carbide concerned, and is used over the long period of time and it may result in breakage depending on the case, it is not desirable.
[0025] As for the honeycomb structure object of this invention, it is desirable that metal silicon is included as a binding material for combining these silicon carbide particle with the silicon carbide particle from which the nature porous body of silicon carbide which constitutes this serves as the aggregate. By this, it can be made to be able to sinter at comparatively low sintering temperature at the time of that manufacture, and can consider as the honeycomb structure object which has the thermal shock resistance which was excellent, without calcinating at very high temperature as shown in JP,6-182227,A. Therefore, it is possible to raise the yield, while holding down a manufacturing cost.
[0026] Moreover, even if it burns the particulate deposited for filter playback when it is used, for example for DPF since it has high thermal conductivity as compared with the conventional structure which used glassiness for association of a fireproof particle by having used metal silicon for association of a silicon carbide particle, local generation of heat which damages a filter does not arise. Furthermore, since this invention is not the cylinder-like-object-with-base-like object of a thick wall as shown in JP,61-13845,B or JP,61-13846,B but a porous honeycomb structure object, it can be used under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.
[0027] Next, the manufacture approach of the honeycomb structure object of this invention is explained. In manufacturing the honeycomb structure object of this invention, first, metal silicon and an organic binder are added in a fireproof particle raw material, it mixes and kneads with a conventional method, and the plastic matter for shaping is obtained.
[0028] Here, as a fireproof particle used in this invention, a silicon carbide particle is used from viewpoints, such as thermal resistance, supposing using the honeycomb structure object to manufacture for DPF often exposed to an elevated temperature at the time of combustion processing of an are recording particulate. in addition -- as the class of suitable fireproof particle for use -- an oxide system -- aluminum2 -- O3, ZrO2, Y2O3, and a carbide system -- SiC and a nitride system -- Si3 -- N4, AlN, other mullites, etc. can be mentioned. In addition, although there is a case containing the impurity of minute amounts, such as Fe, aluminum, and calcium, in the raw material used for fireproof particle metallurgy group silicon including silicon carbide, you may use it as it is and what performed and refined chemical processing of chemical washing etc. may be used.
[0029] in addition, reinforcement and Young's modulus -- the above -- in order to obtain the nature porous body of silicon carbide which is a desirable ratio, the technique using an ingredient with small Young's modulus as a binding material can be mentioned like a metal. The metal silicon used in the honeycomb structure object and its manufacture approach of this invention especially is the binding material which was excellent, in view of thermal resistance, corrosion resistance, the ease of handling, etc. However, since the ratio of the above-mentioned reinforcement and Young's modulus has the microstructure organization of the nature porous body of silicon carbide, and strong correlation, metal silicon should not just only necessarily be used for it, and it needs to optimize the microstructure organization decided from the particle diameter of an ingredient, a presentation, burning temperature, etc.
[0030] Here, metal silicon melts during baking, wets the front face of a silicon carbide particle, and bears the role which combines particles. Although the suitable addition of the metal silicon in the manufacture approach of the honeycomb structure object of this invention changes also with the particle size and the configuration of a silicon carbide particle, it needs to consider as 15 - 40% of the

weight of within the limits to the total quantity of a silicon carbide particle and metal silicon, it is desirable to consider as 15 - 35% of the weight of within the limits, and it is still more desirable to consider as 18 - 32% of the weight of within the limits. When the addition of metal silicon is less than 15 % of the weight, since the effectiveness of the Young's modulus reduction by using metal silicon stops fully showing up, it is not desirable. Moreover, when exceeding 40 % of the weight, since the value of Young's modulus becomes large by the eburnation of an organization, it is not desirable.
[0031] The obtained plastic matter is fabricated in a desired honeycomb configuration by an extrusion method etc. Subsequently, this baking is performed after removing the organic binder which carries out temporary quenching of the acquired Plastic solid, and is contained in a Plastic solid (cleaning). As for temporary quenching, it is desirable to carry out at temperature lower than the temperature which metal silicon fuses. You may once hold at the predetermined temperature of about 150-700 degrees C, and to below 50 degrees C / hr, a programming rate may be made late and, specifically, may carry out temporary quenching in a predetermined temperature region.
[0032] About the technique once held at predetermined temperature, with the class and amount of an organic binder which were used, maintenance or maintenance with the two or more temperature level of only a 1 temperature level is sufficient, and in holding with the two or more temperature level further, even if the same, you may change the holding time mutually. Moreover, between a certain 1 temperature-province regions may be similarly made late about the technique of making a programming rate late, or you may make it late among the two or more division, and, in between the two or more [further] division, a rate may be mutually changed also as the same.
[0033] Although an oxidizing atmosphere is sufficient, in order that it etc. may burn violently with oxygen and may make Plastic solid temperature rise rapidly during temporary quenching about the ambient atmosphere of temporary quenching when many organic binders are contained in a Plastic solid, it is also desirable technique by carrying out by inert atmospheres, such as N2 and Ar, to control the abnormality temperature up of a Plastic solid. Control of this abnormality temperature up is important control when a raw material with a large (weak to a thermal shock) coefficient of thermal expansion is used. It is desirable to carry out temporary quenching of the organic binder in said inert atmosphere, when it adds more than 20 % of the weight (outside **) for example, to the main raw material. Moreover, also when a fireproof particle is what is anxious about the oxidation in an elevated temperature besides a SiC particle, it is desirable to control oxidation of a Plastic solid by performing temporary quenching according to the above inert atmospheres above the temperature from which oxidation begins at least.
[0034] The furnace of identitas or another individual may perform this baking following temporary quenching and it as another process, and it is good also as a continuous process in the same furnace. When carrying out temporary quenching and this baking in a different ambient atmosphere, the former is desirable technique, and from standpoints, such as the total firing time and operation cost of a furnace, the latter technique is also desirable.
[0035] Metal silicon needs to become soft in order to obtain the organization where the fireproof particle was combined with metal silicon. In the manufacture approach of the honeycomb structure object concerning this invention, it is desirable that the operation temperature requirement of this baking is 1400-1600 degrees C. Furthermore, although the optimal burning temperature is determined from a microstructure or a characteristic value, it is still more desirable that it is 1450-1600 degrees C, and it is desirable that it is especially 1450-1550 degrees C. When the operation temperature of this baking is less than 1400 degrees C, since the melting point of metal silicon is 1410 degrees C and it cannot be made into porous structure, it is not desirable. Moreover, since the effectiveness of the Young's modulus reduction by a microstructure organization changing at the temperature exceeding 1600 degrees C, and using metal silicon stops fully showing up, it is not desirable.
[0036] In addition, although the sintered compact of high thermal conductivity is obtained in order to combine the manufacture approach using the recrystallizing method shown in aforementioned JP,6-182228,A by silicon carbide particles Since it sinters by the evaporation condensation device in which it stated previously, in order to evaporate silicon carbide A burning temperature higher than the manufacture approach of this invention is needed, and in order to obtain a practically usable silicon carbide sintered compact, it is usually necessary to calcinate at least 1800 degrees C or more at an

elevated temperature 2000 degrees C or more.

[0037] About the ambient atmosphere of this baking, choosing according to the class of fireproof particle is desirable. Since the silicon carbide particle is used as a fireproof particle in this invention, we are anxious about the oxidation in an elevated temperature. Therefore, in the temperature region beyond the temperature from which oxidation begins at least, it is desirable to consider as non-oxidizing atmospheres, such as N2 and Ar.

[0038]

[Example] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited to these examples.

[0039] (Examples 1 and 2) It blended so that it might become the presentation which shows the SiC raw material powder which has mean particle diameter as shown in Table 1, and metal Si powder with a mean particle diameter of 4 micrometers in this table, and the methyl cellulose 6 weight section, the surfactant 2.5 weight section, and the water 24 weight section were added as an organic binder to this powder 100 weight section, it mixed and kneaded to homogeneity, and the plastic matter for shaping was obtained. The obtained plastic matter was fabricated with the extruding press machine in 0.43mm in the outer diameter of 45mm, die length of 120mm, and septum thickness, and the honeycomb configuration of cel consistency 100 cel / square inch (16 cels / cm2). Baking of 2 hours was performed with the burning temperature which shows this honeycomb Plastic solid in Table 1 in a non-oxidizing atmosphere after performing temporary quenching for cleaning at 550 degrees C in an oxidizing atmosphere for 3 hours, and the silicon carbide sintered compact of honeycomb structure was produced by porosity (examples 1 and 2). The test piece was cut down from each of this sintered compact, and an average pole diameter and porosity were measured in the mercury porosimeter. Furthermore, the material testing machine was used, reinforcement was computed by the four-point bending test, Young's modulus was measured and computed from the relation between a load and the amount of displacement by the static-modulus examining method, and the result was shown in Table 1. Moreover, when the crystal phase was identified in the X diffraction, consisting of SiC and Si was checked.

[0040] (Example 1 of a comparison) The silicon carbide sintered compact of honeycomb structure was produced by porosity on condition that the same actuation as said examples 1 and 2, and the recrystallizing method shown in Table 1 except not using metal Si powder as a raw material (example 1 of a comparison). Furthermore, each physical-properties value was measured and computed by the same, same actuation as said examples 1 and 2, and the result was shown in Table 1. Moreover, when the crystal phase was identified in the X diffraction, consisting only of SiC was checked.

[0041]

[Table 1]

	プロセス	ＳｉＣ粒径 (μm)	組成Ｓｉ/ＳｉＣ比 (wt%)	焼成温度 (℃)	平均細孔径 (μm)	気孔率 (%)	強度 (MPa)	ヤング率 (GPa)	強度 (MPa) ／ヤング率 (GPa) 比
実施例1	金属珪素結合	30	２０／８０	1450	10	45	20	17	1.17
実施例2	金属珪素結合	30	３０／７０	1450	10	45	20	15	1.33
比較例1	再結晶反応焼結	15	０／１００	2300	10	45	40	38	1.05

[0042] (Thermal-shock-resistance trial (water-quenching trial)) After dropping and quenching these samples from the inside of the electric furnace of predetermined temperature to underwater [of a room temperature], using as a sample the test piece cut down from each sintered compact of said examples 1 and 2 and the example 1 of a comparison, the reinforcement of each sample was measured by the four-point bending test. "Room temperature reinforcement" and reinforcement of the sample after quenching were made into "residual reinforcement" for the reinforcement of the sample before heating in an electric furnace here, and the graph which plotted residual reinforcement / room temperature reinforcement to temperature-gradient delta[of an electric furnace and water] T (degree C) was shown in drawing 1 .

[0043] To reinforcement beginning to fall from 300 degrees C or more, in examples 1 and 2, it is distinct that reinforcement begins to fall [temperature-gradient deltaT] from 400 degrees C or more, and temperature-gradient deltaT was able to check the thermal shock resistance which was excellent in

this invention in the example 1 of a comparison. Furthermore, when the example 1 was compared with the example 2, as compared with the example 1, the direction of an example 2 had the small degree of a fall on the strength, and was able to check excelling in thermal shock resistance more.
[0044]
[Effect of the Invention] As explained above, since the honeycomb structure object of this invention has set the reinforcement and Young's modulus of the nature porous body of silicon carbide which constitute it as a predetermined ratio, it has the thermal shock resistance which was excellent as compared with the case where it produces by the conventional recrystallizing method. Furthermore, though the silicon carbide particle which is a fireproof particle is included, since it can be made to sinter with a comparatively low burning temperature at the time of the manufacture, while holding down a manufacturing cost, the yield can also improve and it can provide cheaply. Moreover, when it is used for DPF, even if [since it has high thermal conductivity in addition to the outstanding thermal shock resistance for example,] it burns the particulate deposited for filter playback, local generation of heat which damages a filter does not arise. Furthermore, since it is a porous honeycomb structure object, it can be suitably used also under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the honeycomb structure object used for a filter, catalyst support, etc. for automobile exhaust purification, and its manufacture approach.

PRIOR ART

[Description of the Prior Art] The porous honeycomb structure object is widely used as catalyst support for supporting the catalyst component which purifies the filter for carrying out uptake removal of the particulate matter contained in dust-containing fluid like diesel-power-plant exhaust gas, or the harmful matter in exhaust gas. Moreover, using a fireproof particle like a silicon carbide (SiC) particle as a component of such a honeycomb structure object is known.
[0003] As a concrete related technique, the silicon carbide powder which has a predetermined specific surface area and a predetermined impurity content is used as a start raw material, and the nature catalyst support of porosity silicon carbide of the honeycomb structure calcinated and acquired by the configuration of a request of this after shaping and desiccation in a 1600-2200-degree C temperature requirement is indicated by JP,6-182228,A.
[0004] A vitrification material adds to the fireproof constituent which, on the other hand, contains an easy-oxidizable material or an easy-oxidizable material in JP,61-26550,A, and the silicon-carbide Plastic solid with which the manufacture approach of the vitrification material content refractories characterized by to carry out nakedness baking of the Plastic solid mixed, kneaded, and fabricated and fabricated in the furnace of a non-oxidizing atmosphere adds and fabricates an organic binder and the inorganic binder of a clay mineral system, textile glass yarn, and a silicic-acid lithium system to silicon-carbide powder at JP,8-165171,A is indicated with binding material, respectively.
[0005] Moreover, after adding and fabricating binding material, such as glassiness flux or argillaceous, to the silicon carbide particle used as the aggregate as the manufacture approach of the conventional nature sintered compact of porosity silicon carbide, the method of burning, hardening and manufacturing the Plastic solid at the temperature which said binding material fuses is also introduced to said JP,6-182228,A.
[0006] furthermore, to JP,61-13845,B and JP,61-13846,B Silica sand, a pottery grinding object, aluminum2O3, TiO2, the metallic oxide of ZrO2 grade, The fireproof particle by which the particle size regulation was carried out to the predetermined grain size which consists of silicon carbide, a nitride, boride, or other fireproof ingredients The suitable fireproof particle pitch diameter, fireproof particle particle size distribution, tube-like object porosity, a tube-like object average pole diameter,

tube-like object pore volume, tube-like object septum thickness, etc. are indicated about the high-temperature-service ceramic filter formed in the porous cylinder-like-object-with-base-like object with fireproof binding material, such as water glass, a frit, and a cover coat.

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, since the honeycomb structure object of this invention has set the reinforcement and Young's modulus of the nature porous body of silicon carbide which constitute it as a predetermined ratio, it has the thermal shock resistance which was excellent as compared with the case where it produces by the conventional recrystallizing method. Furthermore, though the silicon carbide particle which is a fireproof particle is included, since it can be made to sinter with a comparatively low burning temperature at the time of the manufacture, while holding down a manufacturing cost, the yield can also improve and it can provide cheaply. Moreover, when it is used for DPF, even if [since it has high thermal conductivity in addition to the outstanding thermal shock resistance for example,] it burns the particulate deposited for filter playback, local generation of heat which damages a filter does not arise. Furthermore, since it is a porous honeycomb structure object, it can be suitably used also under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Although a silicon carbide component evaporates from a silicon carbide particle front face, the neck section grows because this condenses in the contact section between particles (neck section), and an integrated state is obtained with the sintering gestalt (necking) by the recrystallization reaction of the silicon carbide powder itself shown in said JP,6-182228,A In order for this to have to cause cost quantity since a very high burning temperature is required, and to evaporate silicon carbide and to have to carry out elevated-temperature baking of the ingredient with a high coefficient of thermal expansion, there was a problem that a baking yield fell.
[0008] Furthermore, while it is possible to obtain the porous body of high intensity according to the aforementioned approach, it will originate in the physical property of the silicon carbide which is an ingredient, and the porous body which shows a numeric value with high Young's modulus will be obtained.
[0009] Generally, a heat-resistant impact destructive drag coefficient (R) is shown by the following formula (1). Here, for S, disruptive strength and nu are [Young's modulus and alpha of a Poisson's ratio and E] coefficients of thermal expansion. nu and alpha are the numeric values of an ingredient proper, and if it is the same ingredient, while most change is values which are not accepted, they is numeric values sharply changed by the porosity of the ingredient, a microstructure organization, etc. about S and E.
R=S(1-nu)/Ealpha -- (1)
[0010] Although thermal shock resistance was proportional to reinforcement as the above-mentioned formula (1) was shown, by the manufacture approach of the sintered compact shown in JP,6-182228,A since it is in inverse proportion to Young's modulus, there was a problem that the sintered compact which has sufficient thermal shock resistance could not be manufactured even if it is high intensity, since the value of Young's modulus becomes high.
[0011] The technique of on the other hand combining the coal-for-coke-making-ized silicon powder shown in JP,61-26550,A or JP,6-182228,A by glassiness Although it is low and ends with 1000-1400 degrees C as a burning temperature for example, in using as an ingredient of the diesel particulate filter (DPF) for removing the particulate contained in the exhaust gas discharged from a diesel power plant in the sintered compact produced by this technique When it was going to burn the particulate which the collection was carried out to the filter and deposited for filter playback, since thermal conductivity was small, there was a trouble that local generation of heat arose.

[0012] Furthermore, although the filter shown in JP,61-13845,B and JP,61-13846,B was porosity, septa are 5-20mm and a thick cylinder-like-object-with-base-like object, and were not able to apply it to the bottom of a high SV (space velocity) condition like the filter for automobile exhaust purification.
[0013] This invention has high reinforcement and thermal shock resistance, and aims at offering the honeycomb structure object which can be suitably used also under high SV conditions as the filter for automobile exhaust purification, or catalyst support by processing of ****** etc., and its manufacture approach while being able to manufacture it cheaply with a comparatively low burning temperature, though it is made in view of such a conventional situation and a fireproof particle like a silicon carbide particle is included.

MEANS

[Means for Solving the Problem] That is, according to this invention, it is the honeycomb structure object which has the circulation hole of a large number penetrated to the shaft orientations divided by the septum which consists of a nature porous body of silicon carbide, and the honeycomb structure object characterized by the reinforcement and Young's modulus of said nature porous body of silicon carbide filling the following relation is offered.
[Equation 4] Reinforcement (MPa) / Young's modulus (GPa) >=1.1[0015] In this invention, it is desirable that the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation.
[Equation 5]
Reinforcement (MPa) / Young's modulus (GPa) >=1.25[0016] Furthermore, in this invention, it is desirable that the reinforcement and Young's modulus of said nature porous body of silicon carbide fill the following relation. In addition, in this invention, it is desirable that the silicon carbide particle from which the nature porous body of silicon carbide serves as the aggregate, and the metal silicon with which it becomes binding material are included.
[Equation 6] Reinforcement (MPa) / Young's modulus (GPa) >=1.3[0017] On the other hand, according to this invention, add metal silicon and an organic binder in a silicon carbide particle raw material, and the plastic matter mixed, and kneaded and obtained is fabricated in a honeycomb configuration. In the manufacture approach of the honeycomb structure object which carries out actual baking after carrying out temporary quenching of the acquired Plastic solid and removing the organic binder in this Plastic solid The manufacture approach of the honeycomb structure object characterized by the addition of said metal silicon being 15 - 40% of the weight of the range to the total quantity of said silicon carbide particle raw material and metal silicon is offered.
[0018] In addition, in this invention, it is desirable to carry out this baking in a 1400-1600-degree C temperature requirement.
[0019]
[Embodiment of the Invention] The honeycomb structure object of this invention is constituted by the nature porous body of silicon carbide, and it is set up and produced so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the following relation.
[Equation 7] Reinforcement (MPa) / Young's modulus (GPa) >=1.1[0020] As mentioned above, thermal shock resistance is important in order that holding down the value of Young's modulus as compared with a strong value since it is in inverse proportion to the value of Young's modulus may improve the thermal shock resistance of a honeycomb structure object. If it is going to burn the particulate which thermal shock resistance was [the particulate] low when the above-mentioned numeric value was less than 1.1, for example, the collection was carried out to the filter for filter playback when it used as a diesel particulate filter (DPF) for removing the particulate contained in the exhaust gas discharged from a diesel power plant in this ingredient, and was deposited, since there is a possibility of damaging depending on the case, according to the rapid temperature gradient produced in a filter, it is not desirable. In the honeycomb structure object concerning this invention, since the ratio of the reinforcement which is the physical-properties value of the nature porous body of silicon carbide which constitutes it, and Young's modulus is set as the relation of the above-mentioned

formula, the outstanding thermal shock resistance is shown.
[0021] Moreover, if it sets up so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the following relation, since still better thermal shock resistance is obtained, it is desirable.
[Equation 8]
Reinforcement (MPa) / Young's modulus (GPa) >=1.25[0022] Furthermore, if it sets up so that the reinforcement and Young's modulus of the nature porous body of silicon carbide may fill the following relation, especially since sufficient thermal shock resistance is obtained, it is desirable.
[Equation 9] Reinforcement (MPa) / Young's modulus (GPa) >=1.3[0023] In addition, when using the honeycomb structure object concerned as DPF etc. is assumed, the reinforcement of the nature porous body of silicon carbide and the relation of Young's modulus can be used satisfactory, if it sets up so that the following type may be filled in general.
[Equation 10]
Reinforcement (MPa) / Young's modulus (GPa) <=4.0[0024] Since distortion becomes gradually large in the process which distortion may produce in the honeycomb structure constituted by that Young's modulus is low although it is desirable from a viewpoint of thermal shock resistance when the numeric value in the above-mentioned formula exceeds 4.0 by the nature porous body of the silicon carbide concerned, and is used over the long period of time and it may result in breakage depending on the case, it is not desirable.
[0025] As for the honeycomb structure object of this invention, it is desirable that metal silicon is included as a binding material for combining these silicon carbide particle with the silicon carbide particle from which the nature porous body of silicon carbide which constitutes this serves as the aggregate. By this, it can be made to be able to sinter at comparatively low sintering temperature at the time of that manufacture, and can consider as the honeycomb structure object which has the thermal shock resistance which was excellent, without calcinating at very high temperature as shown in JP,6-182227,A. Therefore, it is possible to raise the yield, while holding down a manufacturing cost.
[0026] Moreover, even if it burns the particulate deposited for filter playback when it is used, for example for DPF since it has high thermal conductivity as compared with the conventional structure which used glassiness for association of a fireproof particle by having used metal silicon for association of a silicon carbide particle, local generation of heat which damages a filter does not arise. Furthermore, since this invention is not the cylinder-like-object-with-base-like object of a thick wall as shown in JP,61-13845,B or JP,61-13846,B but a porous honeycomb structure object, it can be used under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.
[0027] Next, the manufacture approach of the honeycomb structure object of this invention is explained. In manufacturing the honeycomb structure object of this invention, first, metal silicon and an organic binder are added in a fireproof particle raw material, it mixes and kneads with a conventional method, and the plastic matter for shaping is obtained.
[0028] Here, as a fireproof particle used in this invention, a silicon carbide particle is used from viewpoints, such as thermal resistance, supposing using the honeycomb structure object to manufacture for DPF often exposed to an elevated temperature at the time of combustion processing of an are recording particulate. in addition -- as the class of suitable fireproof particle for use -- an oxide system -- aluminum2 -- O3, ZrO2, Y2O3, and a carbide system -- SiC and a nitride system -- Si3 -- N4, AlN, other mullites, etc. can be mentioned. In addition, although there is a case containing the impurity of minute amounts, such as Fe, aluminum, and calcium, in the raw material used for fireproof particle metallurgy group silicon including silicon carbide, you may use it as it is and what performed and refined chemical processing of chemical washing etc. may be used.
[0029] in addition, reinforcement and Young's modulus -- the above -- in order to obtain the nature porous body of silicon carbide which is a desirable ratio, the technique using an ingredient with small Young's modulus as a binding material can be mentioned like a metal. The metal silicon used in the honeycomb structure object and its manufacture approach of this invention especially is the binding material which was excellent, in view of thermal resistance, corrosion resistance, the ease of handling, etc. However, since the ratio of the above-mentioned reinforcement and Young's modulus has the microstructure organization of the nature porous body of silicon carbide, and strong correlation, metal

silicon should not just only necessarily be used for it, and it needs to optimize the microstructure organization decided from the particle diameter of an ingredient, a presentation, burning temperature, etc.

[0030] Here, metal silicon melts during baking, wets the front face of a silicon carbide particle, and bears the role which combines particles. Although the suitable addition of the metal silicon in the manufacture approach of the honeycomb structure object of this invention changes also with the particle size and the configuration of a silicon carbide particle, it needs to consider as 15 - 40% of the weight of within the limits to the total quantity of a silicon carbide particle and metal silicon, it is desirable to consider as 15 - 35% of the weight of within the limits, and it is still more desirable to consider as 18 - 32% of the weight of within the limits. When the addition of metal silicon is less than 15 % of the weight, since the effectiveness of the Young's modulus reduction by using metal silicon stops fully showing up, it is not desirable. Moreover, when exceeding 40 % of the weight, since the value of Young's modulus becomes large by the eburnation of an organization, it is not desirable.

[0031] The obtained plastic matter is fabricated in a desired honeycomb configuration by an extrusion method etc. Subsequently, this baking is performed after removing the organic binder which carries out temporary quenching of the acquired Plastic solid, and is contained in a Plastic solid (cleaning). As for temporary quenching, it is desirable to carry out at temperature lower than the temperature which metal silicon fuses. You may once hold at the predetermined temperature of about 150-700 degrees C, and to below 50 degrees C / hr, a programming rate may be made late and, specifically, may carry out temporary quenching in a predetermined temperature region.

[0032] About the technique once held at predetermined temperature, with the class and amount of an organic binder which were used, maintenance or maintenance with the two or more temperature level of only a 1 temperature level is sufficient, and in holding with the two or more temperature level further, even if the same, you may change the holding time mutually. Moreover, between a certain 1 temperature-province regions may be similarly made late about the technique of making a programming rate late, or you may make it late among the two or more division, and, in between the two or more [further] division, a rate may be mutually changed also as the same.

[0033] Although an oxidizing atmosphere is sufficient, in order that it etc. may burn violently with oxygen and may make Plastic solid temperature rise rapidly during temporary quenching about the ambient atmosphere of temporary quenching when many organic binders are contained in a Plastic solid, it is also desirable technique by carrying out by inert atmospheres, such as N2 and Ar, to control the abnormality temperature up of a Plastic solid. Control of this abnormality temperature up is important control when a raw material with a large (weak to a thermal shock) coefficient of thermal expansion is used. It is desirable to carry out temporary quenching of the organic binder in said inert atmosphere, when it adds more than 20 % of the weight (outside **) for example, to the main raw material. Moreover, also when a fireproof particle is what is anxious about the oxidation in an elevated temperature besides a SiC particle, it is desirable to control oxidation of a Plastic solid by performing temporary quenching according to the above inert atmospheres above the temperature from which oxidation begins at least.

[0034] The furnace of identitas or another individual may perform this baking following temporary quenching and it as another process, and it is good also as a continuous process in the same furnace. When carrying out temporary quenching and this baking in a different ambient atmosphere, the former is desirable technique, and from standpoints, such as the total firing time and operation cost of a furnace, the latter technique is also desirable.

[0035] Metal silicon needs to become soft in order to obtain the organization where the fireproof particle was combined with metal silicon. In the manufacture approach of the honeycomb structure object concerning this invention, it is desirable that the operation temperature requirement of this baking is 1400-1600 degrees C. Furthermore, although the optimal burning temperature is determined from a microstructure or a characteristic value, it is still more desirable that it is 1450-1600 degrees C, and it is desirable that it is especially 1450-1550 degrees C. When the operation temperature of this baking is less than 1400 degrees C, since the melting point of metal silicon is 1410 degrees C and it cannot be made into porous structure, it is not desirable. Moreover, since the effectiveness of the Young's modulus reduction by a microstructure organization changing at the temperature exceeding

1600 degrees C, and using metal silicon stops fully showing up, it is not desirable.
[0036] In addition, although the sintered compact of high thermal conductivity is obtained in order to combine the manufacture approach using the recrystallizing method shown in aforementioned JP,6-182228,A by silicon carbide particles Since it sinters by the evaporation condensation device in which it stated previously, in order to evaporate silicon carbide A burning temperature higher than the manufacture approach of this invention is needed, and in order to obtain a practically usable silicon carbide sintered compact, it is usually necessary to calcinate at least 1800 degrees C or more at an elevated temperature 2000 degrees C or more.
[0037] About the ambient atmosphere of this baking, choosing according to the class of fireproof particle is desirable. Since the silicon carbide particle is used as a fireproof particle in this invention, we are anxious about the oxidation in an elevated temperature. Therefore, in the temperature region beyond the temperature from which oxidation begins at least, it is desirable to consider as non-oxidizing atmospheres, such as N2 and Ar.

EXAMPLE

[Example] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited to these examples.
[0039] (Examples 1 and 2) It blended so that it might become the presentation which shows the SiC raw material powder which has mean particle diameter as shown in Table 1, and metal Si powder with a mean particle diameter of 4 micrometers in this table, and the methyl cellulose 6 weight section, the surfactant 2.5 weight section, and the water 24 weight section were added as an organic binder to this powder 100 weight section, it mixed and kneaded to homogeneity, and the plastic matter for shaping was obtained. The obtained plastic matter was fabricated with the extruding press machine in 0.43mm in the outer diameter of 45mm, die length of 120mm, and septum thickness, and the honeycomb configuration of cel consistency 100 cel / square inch (16 cels / cm2). Baking of 2 hours was performed with the burning temperature which shows this honeycomb Plastic solid in Table 1 in a non-oxidizing atmosphere after performing temporary quenching for cleaning at 550 degrees C in an oxidizing atmosphere for 3 hours, and the silicon carbide sintered compact of honeycomb structure was produced by porosity (examples 1 and 2). The test piece was cut down from each of this sintered compact, and an average pole diameter and porosity were measured in the mercury porosimeter. Furthermore, the material testing machine was used, reinforcement was computed by the four-point bending test, Young's modulus was measured and computed from the relation between a load and the amount of displacement by the static-modulus examining method, and the result was shown in Table 1. Moreover, when the crystal phase was identified in the X diffraction, consisting of SiC and Si was checked.
[0040] (Example 1 of a comparison) The silicon carbide sintered compact of honeycomb structure was produced by porosity on condition that the same actuation as said examples 1 and 2, and the recrystallizing method shown in Table 1 except not using metal Si powder as a raw material (example 1 of a comparison). Furthermore, each physical-properties value was measured and computed by the same, same actuation as said examples 1 and 2, and the result was shown in Table 1. Moreover, when the crystal phase was identified in the X diffraction, consisting only of SiC was checked.
[0041]
[Table 1]

	プロセス	ＳｉＣ粒径 (μm)	組成Ｓｉ/ＳｉＣ比 (wt%)	焼成温度 (℃)	平均細孔径 (μm)	気孔率 (%)	強度 (MPa)	ヤング率 (GPa)	強度 (MPa) /ヤング率 (GPa) 比
実施例1	金属珪素結合	30	２０／８０	1450	10	45	20	17	1.17
実施例2	金属珪素結合	30	３０／７０	1450	10	45	20	15	1.33
比較例1	再結晶反応焼結	15	０／１００	2300	10	45	40	38	1.05

[0042] (Thermal-shock-resistance trial (water-quenching trial)) After dropping and quenching these samples from the inside of the electric furnace of predetermined temperature to underwater [of a room

temperature], using as a sample the test piece cut down from each sintered compact of said examples 1 and 2 and the example 1 of a comparison, the reinforcement of each sample was measured by the four-point bending test. "Room temperature reinforcement" and reinforcement of the sample after quenching were made into "residual reinforcement" for the reinforcement of the sample before heating in an electric furnace here, and the graph which plotted residual reinforcement / room temperature reinforcement to temperature-gradient delta[of an electric furnace and water] T (degree C) was shown in drawing 1 .
[0043] To reinforcement beginning to fall from 300 degrees C or more, in examples 1 and 2, it is distinct that reinforcement begins to fall [temperature-gradient deltaT] from 400 degrees C or more, and temperature-gradient deltaT was able to check the thermal shock resistance which was excellent in this invention in the example 1 of a comparison. Furthermore, when the example 1 was compared with the example 2, as compared with the example 1, the direction of an example 2 had the small degree of a fall on the strength, and was able to check excelling in thermal shock resistance more.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the graph which plotted residual reinforcement / room temperature reinforcement to temperature-gradient delta[of an electric furnace and water] T (degree C).